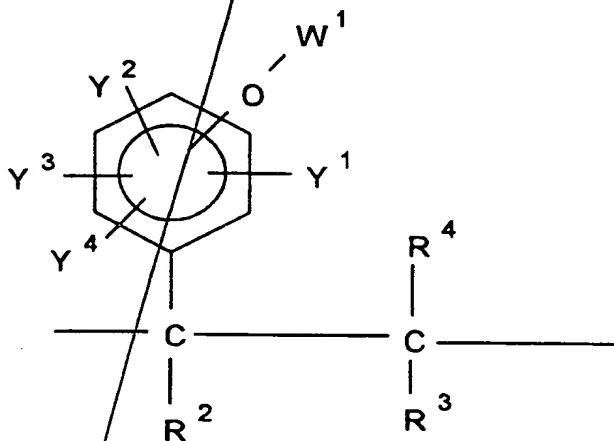


CLAIMS

1. A process for forming over a metal surface an adherent solid coating that imparts to the metal surface after coating at least one of the following changes: (i) protecting the surface as treated, without any additional coating, from corrosion more effectively than does the absence of any coating; (ii) improving the adhesion of a subsequently applied coating, compared to the adhesion that would be achieved between the same subsequently applied coating and the uncoated metallic surface; and (iii) allowing the treated metallic surface to be satisfactorily cold-worked without the need for any liquid organic lubricant under conditions where the metal surface if not coated can not be satisfactorily cold-worked without use of an organic liquid lubricant, said process comprising operations of: (I) coating said metal surface with a layer of an aqueous liquid composition comprising water and:

- (A) a concentration of a component of dissolved phosphorus-containing anions;
- (B) a concentration of a dissolved component selected from the group consisting of simple and complex anions containing fluorine atoms;
- (C) a concentration of a component consisting of dissolved, dispersed, or both dissolved and dispersed materials (α), (β), or both (α) and (β), wherein: (α) consists of polymer molecules each of which has at least one unit conforming to the immediately following general formula (II):

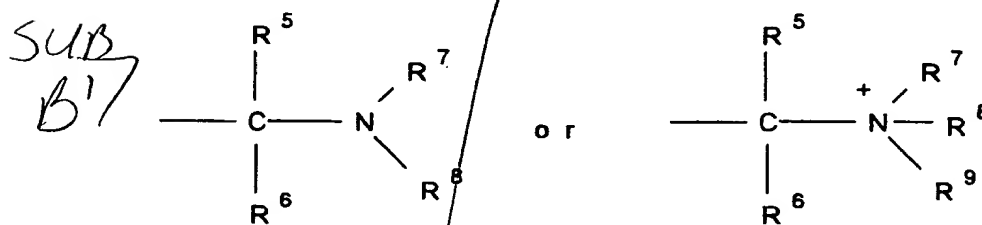


wherein:

- each of R^2 through R^4 is selected, independently of each other and independently from one molecule of the component to another and from one to another unit conforming to this formula when there is more than one such unit in a single polymer molecule, from the group consisting of

a hydrogen moiety, an alkyl moiety with from 1 to 5 carbon atoms, and an aryl moiety with from 6 to 18 carbon atoms;

each of Y¹ through Y⁴ is selected, independently, except as noted further below, of each other and independently from one molecule of the component to another and from one to another unit of any polymer molecule conforming to this formula when there is more than one such unit in a single polymer molecule from the group consisting of: a hydrogen moiety; a -CH₂Cl moiety; an alkyl moiety with from 1 to 18 carbon atoms; an aryl moiety with from 6 to 18 carbon atoms; a moiety conforming to the general formula -CR¹²R¹³OR¹⁴, where each of R¹² through R¹⁴ is selected from the group consisting of a hydrogen moiety, an alkyl moiety, an aryl moiety, a hydroxyalkyl moiety, an aminoalkyl moiety, a mercaptoalkyl moiety, and a phosphoalkyl moiety; and a moiety Z that conforms to one of the two immediately following general formulas:



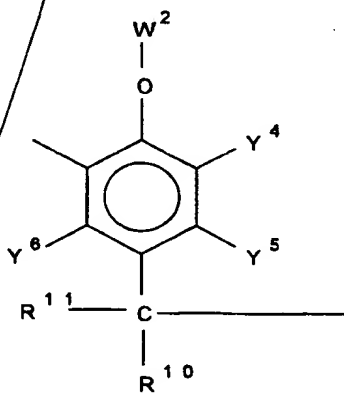
where each of R⁵ through R⁸ is selected, independently of each other and independently from one molecule of the component to another and from one to another unit conforming to this formula when there is more than one such unit in a single polymer molecule, from the group consisting of a hydrogen moiety, an alkyl moiety, an aryl moiety, a hydroxyalkyl moiety, an aminoalkyl moiety, a mercaptoalkyl moiety, and a phosphoalkyl moiety and R⁹ is selected from the group consisting of a hydrogen moiety, an alkyl moiety, an aryl moiety, a hydroxy or polyhydroxy alkyl moiety, an amino or polyamino alkyl moiety, a mercapto or polymercapto alkyl moiety, a phospho or polyphospho alkyl moiety, an -O⁻ moiety, and an -OH moiety,

at least one of Y¹ through Y⁴ in at least one unit of each selected polymer

molecule being a moiety Z as above defined; and

- W^1 is selected, independently from one molecule of the component to another and from one to another unit conforming to this formula when there is more than one such unit in a single polymer molecule, from the group consisting of a hydrogen moiety, an acyl moiety, an acetyl moiety, a benzoyl moiety; a 3-allyloxy-2-hydroxypropyl moiety; a 3-benzyloxy-2-hydroxypropyl moiety; a 3-butoxy-2-hydroxypropyl moiety; a 3-alkyloxy-2-hydroxypropyl moiety; a 2-hydroxyoctyl moiety; a 2-hydroxyalkyl moiety; a 2-hydroxy-2-phenylethyl moiety; a 2-hydroxy-2-alkylphenylethyl moiety; a benzyl, methyl, ethyl, propyl, unsubstituted alkyl, or unsubstituted allyl, unsubstituted alkylbenzyl moiety; a halo or polyhalo alkyl, or halo or polyhalo alkenyl moiety; a moiety derived from a condensation polymerization product of ethylene oxide, propylene oxide or a mixture thereof by deleting one hydrogen atom therefrom; and a sodium, potassium, lithium, ammonium or substituted ammonium, or phosphonium or substituted phosphonium cation moiety; and

(β) consists of polymer molecules each of which does not include a unit conforming to general formula (II) as given above but does include at least one unit corresponding to the immediately following general formula (III):



wherein:

- each of R^{10} and R^{11} is selected, independently of each other and independently from one molecule of the component to another and from one to another unit conforming to this formula when there is more than

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B1

one such unit in a single polymer molecule, from the group consisting of a hydrogen moiety, an alkyl moiety with from 1 to 5 carbon atoms, and an aryl moiety with from 6 to 18 carbon atoms;

- each of Y^4 through Y^6 is selected, independently of each other and independently from one molecule of the component to another and from one to another unit of any polymer molecule conforming to this formula when there is more than one such unit in a single polymer molecule, except as noted further below, from the group consisting of: a hydrogen moiety; a $-CH_2Cl$ moiety; an alkyl moiety with from 1 to 18 carbon atoms; an aryl moiety with from 6 to 18 carbon atoms; a moiety conforming to the general formula $-CR^{12}R^{13}OR^{14}$, where each of R^{12} through R^{14} is selected from the group consisting of a hydrogen moiety, an alkyl moiety, an aryl moiety, a hydroxyalkyl moiety, an aminoalkyl moiety, a mercaptoalkyl moiety, and a phosphoalkyl moiety; and a moiety Z as defined for material (α) above, at least one of Y^1 through Y^4 in at least one unit of each selected polymer molecule being a moiety Z as above defined; and

W^2 is selected, independently from one molecule of the component to another and from one to another unit of any polymer molecule conforming to this formula when there is more than one such unit in a single polymer molecule, from the group consisting of a hydrogen moiety, an acyl moiety, an acetyl moiety, a benzoyl moiety; a 3-allyloxy-2-hydroxypropyl moiety; a 3-benzyloxy-2-hydroxypropyl moiety; a 3-butoxy-2-hydroxypropyl moiety; a 3-alkyloxy-2-hydroxypropyl moiety; a 2-hydroxyoctyl moiety; a 2-hydroxyalkyl moiety; a 2-hydroxy-2-phenylethyl moiety; a 2-hydroxy-2-alkylphenylethyl moiety; a benzyl, methyl, ethyl, propyl, unsubstituted alkyl, unsubstituted allyl, or unsubstituted alkylbenzyl moiety; a halo or polyhalo alkyl, or halo or polyhalo alkenyl, moiety; a moiety derived from a condensation polymerization product of ethylene oxide, propylene oxide or a mixture thereof by deleting one hydrogen atom therefrom; and a sodium, potassium, lithium, ammonium or substituted ammonium, or phosphonium or substituted phosphonium cation moiety;

the phrase "polymer molecule" in the above definitions of materials (α) and (β) including any electrically neutral molecule with a molecular weight of at least 300 daltons; and

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(D) a concentration of a component of dissolved, stably dispersed, or both dissolved and stably dispersed film-forming molecules, said molecules not being part of any of immediately previously recited components (A) through (C);

and (II) drying into place over the metal surface the non-volatile contents of the liquid layer formed in operation (I), so as to form said solid coating.

2. A process according to claim 1, wherein:

- the solid layer formed in operation (II) has a mass per unit area of the metal surface coated that is from about 0.2 to about 10 grams per square meter (g/m^2);

- either:

- component (B) includes at least one of the elements boron, silicon, titanium, zirconium, and hafnium in anions that also contain fluorine atoms, and the concentration, in a unit of moles per aqueous liquid composition volume, of the total of the elements boron, silicon, titanium, zirconium, and hafnium in the liquid composition from which a layer is formed in step (I) has a ratio to the concentration of phosphorus atoms that is stoichiometrically equivalent to the concentration of component (A) in said aqueous liquid composition, in the same unit as for component (B), that is from about 0.03:1.0 to about 2.0:1.0; or

- component (B) does not include any of the elements boron, silicon, titanium, zirconium and hafnium, and the the concentration in moles of fluorine atoms in the liquid composition from which a layer is formed in step (I) has a ratio to the concentration in moles of phosphorus atoms that is stoichiometrically equivalent to the concentration of component (A) in the same mass of the same liquid composition that is from about 0.3:1.0 to about 7:1.0;

- in said aqueous liquid composition, the concentration of component (C), in a unit of mass per aqueous liquid composition volume, has a ratio to the stoichiometrically equivalent concentration as H_3PO_4 of component (A), in the same unit as for component (C), that is from about 0.02:1.0 to about 2.0:1.0;

- in said aqueous liquid composition, the concentration of component (D), in a unit of mass per volume of the total liquid composition, has a ratio to the concentration of component (A) in the same unit as for component (D) that is from about 0.3:1.0 to about 15:1.0; and

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- the liquid composition also contains a volume of a component (E) of stably dispersed solid material that in isolated form has a coefficient of static friction, measured between two pieces of the solid material itself or between the solid material and cold rolled steel, that is not greater than 0.35, this solid material not being part of any of components (A) through (D), the volume of component (E) in said aqueous liquid composition being such that an equal volume of high density polyethylene has a mass with a ratio to the mass of component (D) present in the same liquid composition that is from about 0.005:1.0 to about 0.40:1.0.
3. A process according to claim 2, wherein:
- component (A) was provided to the composition as orthophosphoric acid or at least one salt thereof;
 - component (B) is selected from the group consisting of anions with one of the chemical formulas BF_4^{-1} , SiF_6^{-2} , TiF_6^{-2} , ZrF_6^{-2} , and HfF_6^{-2} ;
 - component (C) is selected from molecules of type (α) when:
 - each of R^2 through R^6 , R^{10} , R^{11} , W^1 , and W^2 is a hydrogen atom moiety;
 - each of Y^1 through Y^6 is a hydrogen atom moiety or a moiety Z;
 - averaged over the entire content of component (C), each polymer molecule contains a number of units corresponding to general formulas (II) as defined above that is from about 5 to about 50;
 - averaged over the entire content of component (C), the number of moieties Z has a ratio to the number of aromatic nuclei that is from about 0.20:1.0 to about 2.0:1.0;
 - averaged over the entire content of component (C), the number of polyhydroxyl moieties Z, which are defined as those moieties Z in which at least R^8 in the general formulas for moieties Z has (i) from 4 to 6 carbon atoms and (ii) as many hydroxyl groups, each attached to a distinct one of the carbon atoms, as one less than the number of carbon atoms in the R^8 moiety, has a ratio to the total number of moieties Z in the composition that is at least about 0.50:1.0; and
 - R^7 is an alkyl moiety with not more than 3 carbon atoms.
4. A process according to claim 3, wherein:
- the solid layer formed in operation (II) has a mass per unit area of the metal surface coated that is from about 0.80 to about 4.0 g/m²;
 - component (B) includes at least one of the elements boron, silicon, titanium, zir-

conium, and hafnium in anions that also contain fluorine atoms, and the concentration in a unit of moles per aqueous liquid composition volume of the total of the elements boron, silicon, titanium, zirconium, and hafnium in the liquid composition from which a layer is formed in step (I) has a ratio to the concentration of phosphorus atoms that is stoichiometrically equivalent to the concentration of component (A), in the same unit as for component (B), is from about 0.12:1.0 to about 0.40:1.0;

- in said aqueous liquid composition, the concentration of component (C), in a unit of mass per volume, has a ratio to the stoichiometrically equivalent concentration as H_3PO_4 of component (A), in the same unit as for component (C), that is from about 0.08:1.0 to about 0.40:1.0;

- in said aqueous liquid composition, the concentration of component (D), in a unit of mass per volume of the total liquid composition, has a ratio to the concentration of component (A) in the same unit as for component (D) that is from about 0.9:1.0 to about 4.0:1.0; and

- the liquid composition also contains a volume of component (E) of stably dispersed solid material that in isolated form has a coefficient of static friction, measured between two pieces of the solid material itself or between the solid material and cold rolled steel, that is not greater than 0.16, this solid material not being part of any of components (A) through (D), the volume of component (E) being such that an equal volume of high density polyethylene has a mass with a ratio to the mass of component (D) present in the same liquid composition that is from about 0.025:1.0 to about 0.10:1.0.

5. A process according to claim 4, wherein:

- the solid layer formed in operation (II) has a mass per unit area of the metal surface coated that is from about 1.5 to about 2.5 g/m²;

- in said aqueous liquid composition, component (B) is hexafluorotitanic acid, and its concentration in a unit of moles of titanium per volume of said liquid composition has a ratio to the concentration of phosphorus atoms that is stoichiometrically equivalent to the concentration of component (A), in the same unit as for component (B), that is from about 0.21:1.0 to about 0.35:1.0;

- component (C) is selected from polymers of 4-vinyl phenol to which have been grafted Z moieties from reaction of formaldehyde and N-methyl glucamine, and the concentration of component (C), in a unit of mass per volume, has a ratio to

543
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the stoichiometrically equivalent concentration as H_3PO_4 of component (A), in the same unit as for component (C), that is from about 0.14:1.0 to about 0.35:1.0;

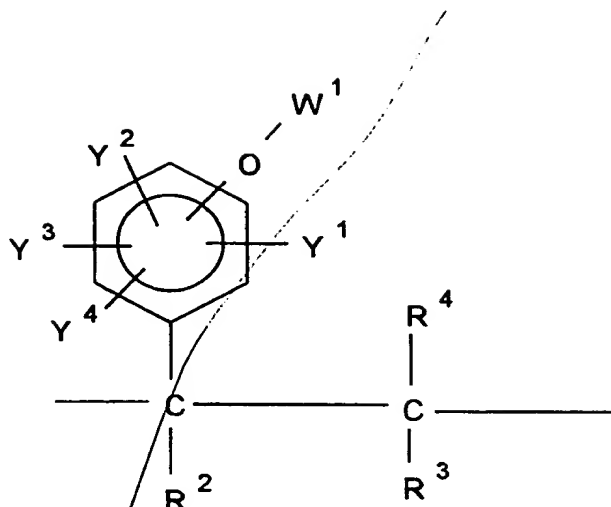
- in said aqueous liquid composition, the concentration of component (D), in a unit of mass per volume of the total liquid composition, has a ratio to the concentration of component (A) in the same unit as for component (D) that is from about 1.5:1.0 to about 2.9:1.0; and

- component (E) is high density polyethylene and has a mass with a ratio to the mass of component (D) present in the same liquid composition that is from about 0.042:1.0 to about 0.10:1.0.

10 ~~6.~~ A process for forming over a metal surface an adherent solid coating that imparts to the metal surface after coating at least one of the following changes: (i) protecting the surface as treated, without any additional coating, from corrosion more effectively than does the absence of any coating; (ii) improving the adhesion of a subsequently applied coating, compared to the adhesion that would be achieved between the same subsequently applied coating and the uncoated metallic surface; and (iii) allowing the treated metallic surface to be satisfactorily cold-worked without the need for any liquid organic lubricant under conditions where the metal surface if not coated can not be satisfactorily cold-worked without use of an organic liquid lubricant, said process comprising operations of: (I) coating said metal surface with a layer of an aqueous liquid composition that has been made by mixing a first mass of water and:

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- (A) a second mass of a water soluble source of phosphorus-containing anions;
 - (B) a third mass of a source of water soluble anions selected from the group consisting of simple and complex anions containing fluorine atoms;
 - (C) a fourth mass of a component consisting of materials (α), (β), or both (α) and (β)
- 25 wherein:

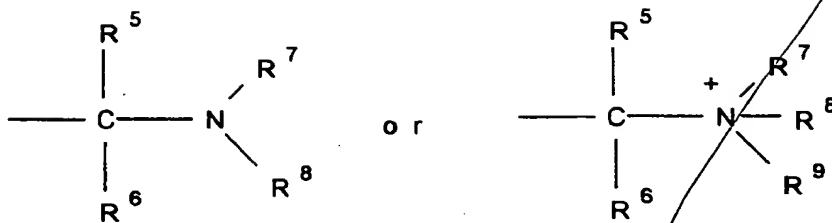
(α) consists of polymer molecules each of which has at least one unit conforming to the immediately following general formula (II):



wherein:

- each of R^2 through R^4 is selected, independently of each other and independently from one molecule of the component to another and from one to another unit conforming to this formula when there is more than one such unit in a single polymer molecule, from the group consisting of a hydrogen moiety, an alkyl moiety with from 1 to 5 carbon atoms, and an aryl moiety with from 6 to 18 carbon atoms;
- each of Y^1 through Y^4 is selected, independently, except as noted further below, of each other and independently from one molecule of the component to another and from one to another unit of any polymer molecule conforming to this formula when there is more than one such unit in a single polymer molecule from the group consisting of: a hydrogen moiety; a $-\text{CH}_2\text{Cl}$ moiety; an alkyl moiety with from 1 to 18 carbon atoms; an aryl moiety with from 6 to 18 carbon atoms; a moiety conforming to the general formula $-\text{CR}^{12}\text{R}^{13}\text{OR}^{14}$, where each of R^{12} through R^{14} is selected from the group consisting of a hydrogen moiety, an alkyl moiety, an aryl moiety, a hydroxyalkyl moiety, an aminoalkyl moiety, a mercaptoalkyl moiety, and a phosphoalkyl moiety; and a moiety Z that conforms to one of the two immediately following general formulas:

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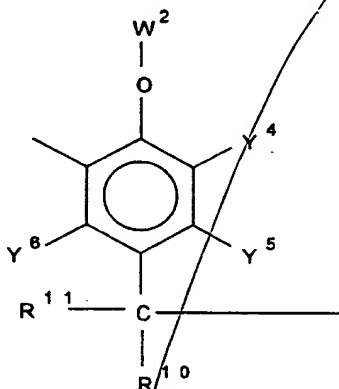
where each of R⁵ through R⁸ is selected, independently of each other and independently from one molecule of the component to another and from one to another unit conforming to this formula when there is more than one such unit in a single polymer molecule, from the group consisting of a hydrogen moiety, an alkyl moiety, an aryl moiety, a hydroxyalkyl moiety, an aminoalkyl moiety, a mercaptoalkyl moiety, and a phosphoalkyl moiety and R⁹ is selected from the group consisting of a hydrogen moiety, an alkyl moiety, an aryl moiety, a hydroxy or polyhydroxy alkyl moiety, an amino or polyamino alkyl moiety, a mercapto or polymercapto alkyl moiety, a phospho or polyphospho alkyl moiety, an -O⁻ moiety, and an -OH moiety,

at least one of Y¹ through Y⁴ in at least one unit of each selected polymer molecule being a moiety Z as above defined; and

- W¹ is selected, independently from one molecule of the component to another and from one to another unit conforming to this formula when there is more than one such unit in a single polymer molecule, from the group consisting of a hydrogen moiety, an acyl moiety, an acetyl moiety, a benzoyl moiety; a 3-allyloxy-2-hydroxypropyl moiety; a 3-benzyloxy-2-hydroxypropyl moiety; a 3-butoxy-2-hydroxypropyl moiety; a 3-alkyloxy-2-hydroxypropyl moiety; a 2-hydroxyoctyl moiety; a 2-hydroxyalkyl moiety; a 2-hydroxy-2-phenylethyl moiety; a 2-hydroxy-2-alkylphenylethyl moiety; a benzyl, methyl, ethyl, propyl, unsubstituted alkyl, unsubstituted allyl, or unsubstituted alkylbenzyl moiety; a halo or polyhalo alkyl, or halo or polyhalo alkenyl moiety; a moiety derived from a condensation polymerization product of ethylene oxide, propylene oxide or a mixture thereof by deleting one hydrogen atom therefrom; and a sodium, potassium, lithium,

ammonium or substituted ammonium, or phosphonium or substituted phosphonium cation moiety; and

(β) consists of polymer molecules each of which does not include a unit conforming to general formula (II) as given above but does include at least one unit corresponding to the immediately following general formula (III):



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wherein:

- each of R^{10} and R^{11} is selected, independently of each other and independently from one molecule of the component to another and from one to another unit conforming to this formula when there is more than one such unit in a single polymer molecule, from the group consisting of a hydrogen moiety, an alkyl moiety with from 1 to 5 carbon atoms, and an aryl moiety with from 6 to 18 carbon atoms;
- each of Y^4 through Y^6 is selected, independently of each other and independently from one molecule of the component to another and from one to another unit of any polymer molecule conforming to this formula when there is more than one such unit in a single polymer molecule, except as noted further below, from the group consisting of: a hydrogen moiety; a $-CH_2Cl$ moiety; an alkyl moiety with from 1 to 18 carbon atoms; an aryl moiety with from 6 to 18 carbon atoms; a moiety conforming to the general formula $-CR^{12}R^{13}OR^{14}$, where each of R^{12} through R^{14} is selected from the group consisting of a hydrogen moiety, an alkyl moiety, an aryl moiety, a hydroxyalkyl moiety, an aminoalkyl moiety, a mercaptoalkyl moiety, and a phosphoalkyl moiety; and a moiety Z as defined for material (α) above, at least one of Y^1 through Y^4 in at least one unit of each selected polymer molecule being a moiety Z as above defined; and

5 - W^2 is selected, independently from one molecule of the component to another and from one to another unit of any polymer molecule conforming to this formula when there is more than one such unit in a single polymer molecule, from the group consisting of a hydrogen moiety, an acyl moiety, an acetyl moiety, a benzoyl moiety; a 3-allyloxy-2-hydroxypropyl moiety; a 3-benzyloxy-2-hydroxypropyl moiety; a 3-butoxy-2-hydroxypropyl moiety; a 3-alkyloxy-2-hydroxypropyl moiety; a 2-hydroxyoctyl moiety; a 2-hydroxyalkyl moiety; a 2-hydroxy-2-phenylethyl moiety; a 2-hydroxy-2-alkylphenylethyl moiety; a benzyl, methyl, ethyl, propyl, unsubstituted alkyl, unsubstituted allyl, or unsubstituted alkylbenzyl moiety; a halo or polyhalo alkyl, or halo or polyhalo alkenyl, moiety; a moiety derived from a condensation polymerization product of ethylene oxide, propylene oxide or a mixture thereof by deleting one hydrogen atom therefrom; and a sodium, potassium, lithium, ammonium or substituted ammonium, or phosphonium or substituted phosphonium cation moiety; and

10 (D) a fifth mass of a source of dissolved, stably dispersed, or both dissolved and stably dispersed film-forming molecules, said molecules not being part of any of immediately previously recited substances (A) through (C);
and (II) drying in place over the metal surface the non-volatile contents of the liquid
15 layer formed in operation (I), so as to form said solid coating.

20 7. A process according to claim 6, wherein:
- the solid layer formed in operation (II) has a mass per unit area of the metal surface coated that is from about 0.2 to about 10 grams per square meter (g/m^2);
25 - either:
- substance (B) includes at least one of the elements boron, silicon, titanium, zirconium, and hafnium in anions that also contain fluorine atoms, and the third mass contains a number of moles of the total of the elements boron, silicon, titanium, zirconium, and hafnium that has a ratio to the number of moles of phosphorus atoms in said liquid composition that is from about 0.03:1.0 to about 2.0:1.0; or
30 - substance (B) does not include any of the elements boron, silicon, titanium, zirconium and hafnium, and the third mass contains a number of moles of fluorine atoms that has a ratio to the number of moles of

phosphorus atoms corresponding to said second mass that is from about 0.3:1.0 to about 7:1.0;

- the fourth mass has a ratio to the stoichiometrically equivalent mass as H_3PO_4 of the second mass that is from about 0.02:1.0 to about 2.0:1.0;
- 5 - the fifth mass has a ratio to the stoichiometric equivalent mass as H_3PO_4 of the second mass that is from about 0.3:1.0 to about 15:1.0; and
- the liquid composition also contains a volume of a component (E) of stably dispersed solid material that in isolated form has a coefficient of static friction, measured between two pieces of the solid material itself or between the solid material and cold rolled steel, that is not greater than 0.35, this solid material not being
- 10 - part of any of components (A) through (D), the volume of component (E) being such that an equal volume of high density polyethylene has a sixth mass with a ratio to said fifth mass that is from about 0.005:1.0 to about 0.40:1.0.

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8. A process according to claim 7, wherein:

- 15 - component (A) was provided to the composition as orthophosphoric acid or at least one salt thereof;
- component (B) is selected from the group consisting of anions with one of the chemical formulas BF_4^{-1} , SiF_6^{-2} , TiF_6^{-2} , ZrF_6^{-2} , and HfF_6^{-2} ;
- component (C) is selected from molecules of type (α) when:
 - 20 - each of R^2 through R^6 , R^{10} , R^{11} , W^1 , and W^2 is a hydrogen atom moiety;
 - each of Y^1 through Y^6 is a hydrogen atom moiety or a moiety Z;
 - averaged over the entire content of component (C), each polymer molecule contains a number of units corresponding to general formulas (II) as defined above that is from about 5 to about 50;
 - 25 - averaged over the entire content of component (C), the number of moieties Z has a ratio to the number of aromatic nuclei that is from about 0.20:1.0 to about 2.0:1.0;
 - averaged over the entire content of component (C), the number of moieties Z in which R^8 in the general formulas for moieties Z has (i) from 4 to 6, carbon atoms and (ii) as many hydroxyl groups, each attached to one
 - 30 - of the carbon atoms, as one less than the number of carbon atoms in the R^8 moiety has a ratio to the total number of moieties Z in the composition that is at least about 0.50:1.0; and
 - R^7 is an alkyl moiety with not more than 3 carbon atoms.

9. A process according to claim 8, wherein:

- the solid layer formed in operation (II) has a mass per unit area of the metal surface coated that is from about 0.80 to about 4.0 g/m²;
- component (B) includes at least one of the elements boron, silicon, titanium, zirconium, and hafnium in anions that also contain fluorine atoms, and the concentration in a unit of moles per aqueous liquid composition volume of the total of the elements boron, silicon, titanium, zirconium, and hafnium in the liquid composition from which a layer is formed in step (I) has a ratio to the concentration of phosphorus atoms that is stoichiometrically equivalent to the concentration of component (A), in the same unit as for component (B), is from about 0.12:1.0 to about 0.40:1.0;
- in said aqueous liquid composition, the concentration of component (C), in a unit of mass per volume, has a ratio to the stoichiometrically equivalent concentration as H₃PO₄ of component (A), in the same unit as for component (C), that is from about 0.08:1.0 to about 0.40:1.0;
- in said aqueous liquid composition, the concentration of component (D), in a unit of mass per volume of the total liquid composition, has a ratio to the concentration of component (A) in the same unit as for component (D) that is from about 0.9:1.0 to about 4.0:1.0; and
- the liquid composition also contains a volume of component (E) of stably dispersed solid material that in isolated form has a coefficient of static friction, measured between two pieces of the solid material itself or between the solid material and cold rolled steel, that is not greater than 0.16, this solid material not being part of any of components (A) through (D), the volume of component (E) being such that an equal volume of high density polyethylene has a mass with a ratio to the mass of component (D) present in the same liquid composition that is from about 0.025:1.0 to about 0.10:1.0.

10. A process according to claim 4, wherein:

- the solid layer formed in operation (II) has a mass per unit area of the metal surface coated that is from about 1.5 to about 2.5 g/m²;
- component (B) is hexafluorotitanic acid, and said third mass contains a number of moles of titanium that has a ratio to the number of moles of phosphorus atoms that is stoichiometrically equivalent to the stoichiometric equivalent as H₃PO₄ of said second mass that is from about 0.21:1.0 to about 0.35:1.0;

- 5
- component (C) is selected from polymers of 4-vinyl phenol to which have been grafted Z moieties from reaction of formaldehyde and N-methyl glucamine, and
 - said fourth mass has a ratio to the stoichiometric equivalent as H_3PO_4 of said second mass that is from about 0.14:1.0 to about 0.35:1.0;
 - said fourth mass has a ratio to the stoichiometric equivalent as H_3PO_4 of said second mass that is from about 1.5:1.0 to about 2.9:1.0; and
 - component (E) is high density polyethylene and said sixth mass has a ratio to said fifth mass that is from about 0.042:1.0 to about 0.10:1.0.

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11. A primary make-up concentrate composition that is suitable for mixing with water and, optionally, one or more other materials to produce an aqueous liquid working composition for use in a process according to any one of claims 1 - 10, said primary make-up concentrate composition comprising water and

- 15
- an amount of component (A) that corresponds stoichiometrically to an amount of H_3PO_4 that constitutes at least about 20 % of the total primary make-up concentrate;
 - at least about 0.50 moles of one or more metal atoms or boron atoms associated with fluorine atoms in an anion per kilogram of the total primary make-up concentrate; and
 - at least about 4.0 percent of component (C).

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12. A primary make-up concentrate according to claim 11, wherein:

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- the amount of component (A) corresponds stoichiometrically to an amount of H_3PO_4 that constitutes at least about 24 % of the total primary make-up concentrate;
 - there is at least about 0.60 mole of one or more metal atoms or boron atoms associated with fluorine atoms in an anion per kilogram of the total primary make-up concentrate; and
 - there is at least about 4.5 percent of component (C).

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13. A primary make-up concentrate according to claim 12, wherein:

- the amount of component (A) corresponds stoichiometrically to an amount of H_3PO_4 that constitutes at least about 28 % of the total primary make-up concentrate;
- there is at least about 0.70 mole of one or more metal atoms or boron atoms associated with fluorine atoms in an anion per kilogram of the total primary make-up concentrate;

- there is at least about 5.0 percent of component (C); and
- component (C) is selected from molecules of type (α) when:
 - each of R^2 through R^6 , R^{10} , R^{11} , W^1 , and W^2 is a hydrogen atom moiety;
 - each of Y^1 through Y^6 is a hydrogen atom moiety or a moiety Z;
 - averaged over the entire content of component (C), each polymer molecule contains a number of units corresponding to general formulas (II) as defined above that is from about 5 to about 50;
 - averaged over the entire content of component (C), the number of moieties Z has a ratio to the number of aromatic nuclei that is from about 0.20:1.0 to about 2.0:1.0;
 - averaged over the entire content of component (C), the number of polyhydroxyl moieties Z, which are defined as those moieties Z in which at least R^8 in the general formulas for moieties Z has (i) from 4 to 6 carbon atoms and (ii) as many hydroxyl groups, each attached to a distinct one of the carbon atoms, as one less than the number of carbon atoms in the R^8 moiety, has a ratio to the total number of moieties Z in the composition that is at least about 0.50:1.0 and
 - R^7 is an alkyl moiety with not more than 3 carbon atoms.

14. A primary make-up concentrate according to claim 13, wherein:

- the amount of component (A) corresponds stoichiometrically to an amount of H_3PO_4 that constitutes at least about 31 % of the total primary make-up concentrate;
- there is at least about 0.80 mole of one or more metal atoms or boron atoms associated with fluorine atoms in an anion per kilogram of the total primary make-up concentrate; and
- there is at least about 5.5 percent of component (C).

15. A primary make-up concentrate according to claim 14, wherein:

- H_3PO_4 constitutes at least about 34 % of the total primary make-up concentrate;
- there is at least about 0.95 mole of hexafluorotitanic acid per kilogram of the total primary make-up concentrate; and
- there is at least about 6.0 percent of polymers of 4-vinyl phenol to which have been grafted Z moieties from reaction of formaldehyde and N-methyl glucamine.

16. A primary make-up concentrate composition that is suitable for mixing with water and, optionally, one or more other materials to produce an aqueous liquid working com-

position for use in a process according to any one of claims 1 - 10, said primary make-up concentrate composition having been made by mixing together a first mass of water and:

- a second mass of a water soluble source of component (A) that corresponds stoichiometrically to a mass of H_3PO_4 that constitutes at least about 20 % of the total primary make-up concentrate;
- a third mass of a water soluble source of anions containing one metal atom or boron atom together with at least four fluorine atoms, said third mass containing at least about 0.50 moles of said metal atoms or boron per kilogram of the total primary make-up concentrate; and
- a fourth mass of component (C) that constitutes at least about 4.0 percent of the total primary make-up concentrate.

17. A primary make-up concentrate according to claim 16, wherein:

- said second mass corresponds stoichiometrically to an amount of H_3PO_4 that constitutes at least about 24 % of the total primary make-up concentrate;
- said third mass contains at least about 0.60 mole of said metal atoms or boron per kilogram of the total primary make-up concentrate; and
- said fourth mass constitutes at least about 4.5 percent of component (C).

18. A primary make-up concentrate according to claim 17, wherein:

- said second mass corresponds stoichiometrically to an amount of H_3PO_4 that constitutes at least about 28 % of the total primary make-up concentrate;
- said third mass contains at least about 0.70 mole of said metal atoms or boron per kilogram of the total primary make-up concentrate;
- said fourth mass constitutes at least about 5.0 percent of component (C); and
- component (C) is selected from molecules of type (α) when:

- each of R^2 through R^6 , R^{10} , R^{11} , W^1 , and W^2 is a hydrogen atom moiety;
- each of Y^1 through Y^6 is a hydrogen atom moiety or a moiety Z;
- averaged over the entire content of component (C), each polymer molecule contains a number of units corresponding to general formulas (II) as defined above that is from about 5 to about 50;
- averaged over the entire content of component (C), the number of moieties Z has a ratio to the number of aromatic nuclei that is from about 0.20:1.0 to about 2.0:1.0;
- averaged over the entire content of component (C), the number of polyhydroxyl moieties Z, which are defined as those moieties Z in which at least

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R⁸ in the general formulas for moieties Z has (i) from 4 to 6 carbon atoms and (ii) as many hydroxyl groups, each attached to a distinct one of the carbon atoms, as one less than the number of carbon atoms in the R⁸ moiety, has a ratio to the total number of moieties Z in the composition that is at least about 0.50:1.0; and

- R⁷ is an alkyl moiety with not more than 3 carbon atoms.

19. A primary make-up concentrate according to claim 18, wherein:

- said second mass corresponds stoichiometrically to an amount of H₃PO₄ that constitutes at least about 31 % of the total primary make-up concentrate;
- said third mass contains at least about 0.80 mole of said metal atoms or boron atoms per kilogram of the total primary make-up concentrate; and
- said fourth mass constitutes at least about 5.5 percent of the total make-up concentrate.

20. A primary make-up concentrate according to claim 19, wherein:

- said second mass consists of H₃PO₄ that constitutes at least about 34 % of the total primary make-up concentrate;
- said third mass contains at least about 0.95 mole of hexafluorotitanic acid per kilogram of the total primary make-up concentrate; and
- said fourth mass consists essentially of at least about 6.0 percent of polymers of 4-vinyl phenol to which have been grafted Z moieties from reaction of formaldehyde and N-methyl glucamine.

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